THE APPLICATION OF ESCHKA'S METHOD TO PIG IRONS.

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OF the three methods generally used for the determination of sulphur in pig iron,—the evolution method, the oxidation method in the wet way, and Bamber's method,—it is generally known that at least two of them are not always accurate.

The evolution method does not, for some irons, give accurate results. The amount of sulphur evolved as hydrogen sulphide plus that remaining unacted on in the residue is less than the amount obtained by either the oxidation or Bamber's method. This error is especially noticeable in those irons containing a high percentage of combined carbon.

The oxidation in the wet way does not, with some irons, effect the complete oxidation of the sulphur, a portion of it remaining with the residue of graphite and silica. Bamber's method is generally used when the oxidation method does not effect its purpose, and no doubt is the safest, besides doing away with the precipitation of the sulphur by barium chloride from a concentrated solution of ferric chloride. When a platinum dish is available, it affords a simple method.

The thought occurred to the writer that if it were possible to reduce the sample of pig iron to a fine powder, its oxidation might be effected in the presence of a basic mixture, such a mixture for example as magnesia and sodium or potassium carbonates. The sulphur, it was hoped, would be converted into soluble sulphates of the bases present, and any small quantity of sulphides of these metals formed could be oxidized by bromine, as in the determination of sulphur in coke. The writer has been informed that v. Reis[1] has already applied this modified Eschka method to pig irons, but his paper is not accessible to me.

Two mixtures were made as follows: One of magnesia 2 parts and sodium carbonate 1 part, well ground and mixed, and another of magnesia 4 parts, potassium carbonate 1 part and sodium carbonate 1 part. The addition of potassium carbonate, it was thought, would hasten the oxidation, potassium carbonate having a slight solvent action on ferric oxide. It was first thought that the samples of pig irons had to be ground very fine, and to accom-

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[1] Stahl und Eisen, 8, 827.

plish this the agate mortar was used, with the result that with a great deal of labor a small sample was finally obtained. Upon treating this sample of about 1 gram with the mixture of magnesium oxide and sodium carbonate, in a platinum crucible at a full red heat, it was found that oxidation was rapid, about fifteen minutes being required to effect it. After a little experimenting it was found that samples of 80 and 60 mesh were oxidized completely, while samples of 30 mesh were not. In fact 50 mesh seemed to be the limit of coarseness of sample.

The samples of basic pig irons as delivered to this laboratory have been crushed in a steel mortar, a pestle and hammer being used. The operation requires about five minutes for a 20-gram sample of 60 mesh. This is done because we wish to have a sample that has been treated under as nearly as possible the same conditions as our basic pig irons. A sample so treated, quite frequently cannot be drilled.

For carrying out the experiments herein described, four samples of gray irons were thus prepared of 80 and 60 mesh each. A given quantity of each iron was all ground to pass through an 80-mesh seive and a 60-mesh sample was prepared in the same way.

No. 1. Gray forge pig iron: Si, 1.22; S (?).

No. 2. Chilled basic pig iron: Si, 0.55; S (?).

No. 3. Sample C of the American Foundrymen's Association: Si, 1.783; S, 0.076.

No. 4. Sample B of same: Si, 1.076; S, 0.056.

The following method was finally decided upon: 3 grams of the sample of a fineness higher than 50 mesh are weighed into a platinum crucible of 30 cc. capacity and 3 grams of the basic mixture are added. The greater part of this mixture is added at once and the whole thoroughly mixed. The balance, about 0.5 gram, is used in covering the top of the mixture. The crucible is then placed over a Bunsen flame, a shield being used to prevent the products of combustion of the flame from coming in contact with the mixture. A description of this shield will be given later. The part of crucible exposed to the flame is heated for one hour at a full red heat. At the end of this time the mass will be found sintered together, and can be broken up when cold with a glass rod, extracted with hot water into a No. 2 beaker, and 10 cc. of bromine water added. It is best to always add a fixed amount as bromine frequently contains sulphur, and by using the same amount in a blank determination this error will be eliminated. The solution is boiled for fifteen minutes on the hot plate and filtered, taking care to see that the filtrate is perfectly clear. The residue is washed with hot water, and to the filtrate 1.5 cc. of concentrated hydrochloric acid are added. The bromine is expelled by boiling, and sulphur is precipitated in the boiling solution by 10 cc. of a hot 10 per cent. solution of barium chloride.

The products of combustion of the gas must be kept away from the contents of the crucible. This can be done without the use of a shield if care is used, at least when gasoline is used for furnishing gas.

It was decided to treat samples Nos. 1 and 2 by each of the following methods:

First. Evolution Method.—Absorption of hydrogen sulphide in solution of potassium hydroxide, oxidation of the potassium sulphide formed by potassium permanganate solution, acidifying with hydrochloric acid, clearing with oxalic acid, neutralizing with ammonia, making slightly acid with hydrochloric acid and precipitation of the sulphur as usual. The sulphur in the residue is determined and added to that obtained as hydrogen sulphide, 10 grams of the sample being used.

Second. Oxidation in the wet way by solution in concentrated nitric acid with the addition of 3 grams of potassium chlorate when solution is complete, and the usual evaporation and resolution with the final precipitation of the sulphur in the 100 cc. solution, using a hot saturated solution of barium chloride and having the ferric chloride solution just short of boiling. The sulphur is determined after standing twelve hours.

Third. Bamber's method as described by Blair, third edition.

SAMPLE NO. 1.

Evolution method + S in residue.	HNO_3 and $KClO_3$.	Bamber's method.	Oxidation in presence of basic mixture.	Time used in igniting.	Fineness of sample.	Mixture used.		Shield.
0.035	0.036	0.035	0.039	1.5 hr.	80 mesh.	MgO &	Na_2CO_3.	No
0.036	0.035	0.036	0.039	1.5 hr.	"	"	"	No
0.036	0.035	0.034	0.040	1 hr.	"	"	"	No
0.035	....	0.035	0.042	1 hr.	"	"	"	No
....	....	0.036	....	....	....	....	....	....
Average:								
0.035	0.035	0.035	0.040	....	....	....	....	....

It was thought that the increase of sulphur as shown by this method was due to the flame, the basic mixture absorbing sulphur therefrom. To prevent this an asbestos board 8 inches by 4 inches was used; in the center of this board and near the lower edge a clean hole was cut, of a size sufficient to admit the crucible for about seven-eighths of its length, and forming a snug fit. To the upper edge of this board was hinged, by means of a copper wire, a board of the same length but 3 inches wide and without any hole. The whole arrangement represents an "A" tent affair, open at both ends, which can be placed over the tripod in such a manner that when the crucible is put into place about seven-eighths of its length projects through the board and rests upon the platinum triangle. The products of combustion from gas pass off above and away from the crucible.

The results obtained on sample No. 1, using the shield, were as follows:

SAMPLE NO. 1.

Nos.	Oxidation in presence of basic mixture.	Fineness of sample.	Time of ignition.	Mixture used.
1	0.0399	60 mesh	$1\frac{1}{2}$ hours	MgO, K_2CO_3 & Na_2CO_3
2	0.0394	"	1 hour	" "
3	0.0385	"	1 "	" "

No. 3 was evaporated to dryness after expelling bromine, redissolved in water slightly acid with hydrochloric acid, and filtered, the sulphur being determined in the filtrate. This, at least, shows that the higher results obtained on this sample were not due to any sulphur absorption from the flame. The use of potassium carbonate shows no decided gain in action or time.

To test the efficiency of the shield, several blank determinations were made with, and without, its use, and the following results obtained.

Three grams of the basic mixture were used and the ignition continued for one hour.

Nos.	Without shield.	With shield.
1	0.0025 gram $BaSO_4$ found	0.0025 gram $BaSO_4$ found
2	0.0024 " " "	0.0025 " " "
3	0.0025 " " "	0.0024 " " "
4	0.0026 " " "	0.0023 " " "

There is evidently no decided advantage in the use of the shield when gasoline gas is used, and care is exercised in igniting the mixture, the flame being kept away from the front or mouth of the crucible. No. 4 of the above, without shield, was ignited so that the flame partly passed by the mouth of the crucible.

The writer is not able to state the value of the shield when ordinary gas is used, but at all events an alcohol lamp of good-sized flame may be safely used.

SAMPLE NO. 2.

Evolution + residue.	HNO_3 and $KClO_3$.	Bamber's method.	Oxidation in presence of basic mixture.	Time of ignition.	Fineness of sample.	Mixture used.	Shield.
0.032	0.032	0.030	0.031	1 hour	60 mesh	MgO, K_2CO_3 & Na_2CO_3	No
0.032	0.030	0.031	0.031	45 min.	"	" "	Yes
0.032	0.030	....	0.032	1 hour	"	" "	Yes
....	0.032	....	....	....	....	....	....

The sulphur was precipitated directly without any previous evaporation to dryness.

In samples Nos. 3 and 4 the sulphur has been determined by the following: 1. Booth, Garrett and Blair; 2. Cramer and Bicknell; 3. Andrew S. McCreath; 4. Albert W. Smith. In the following table their respective numbers are placed after their results.

SAMPLE NO. 3.

Evolution + S in residue.	Chemist's number.	HNO_3 oxidation.	Chemist's number.	Bamber's method.	Chemist's number.	Oxidation in presence of basic mixture.	Fineness.	Time.	Shield.
0.066	1	0.075	2	0.076	1	0.077	60	1 hr.	Yes
....		0.075	3	....		0.076	60	½ hr.	No
....		0.076	4	....		0.076	60	1 hr.	No

SAMPLE NO. 4.

Evolution method + residue.	Chemist's number.	HNO_3 oxidation.	Chemist's number.	Bamber's method.	Chemist's number.	Oxidation in the presence of basic mixture.	Fineness.	Time.	Shield.
0.043	1	0.058	2	0.054	1	0.054	80	1 hr.	No
....		0.055	3	....		0.057	60	1 hr.	Yes
....		0.058	4	....		0.056	60	1 hr.	Yes
....		....		....		0.043[1]	30	1 hr.	Yes

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[1] Results obtained with 30-mesh sample clearly show an incomplete oxidation.

The above samples have all been gray irons. White iron it was thought, on account of its low silicon and absence of graphitic carbon, would not lend itself as readily to oxidation; but samples of white irons, treated in the same way, were oxidized as completely and in the same time as gray.

SAMPLE OF WHITE IRON.

	Per cent. sulphur.	Per cent. sulphur.	Per cent. sulphur.
Bamber's method	0.431	0.432	0.429
Oxidation in basic mixture	0.432	0.430	0.430

This method could no doubt be worked to advantage, using a stream of oxygen and combustion tube. The method does away with the precipitation of the sulphur in the presence of the ferric salt, and the time required for a determination is about that required for the determination of sulphur in coke.

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THE CONSTITUTION OF CAMPHENE.[1]

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THE constitution of camphene is as yet an unsettled point in the chemistry of the terpene series. The objections to the Bredt formula[2] have been stated by Semmler[3] and others, but no satisfactory substitute has been suggested.

As a result of some experiments with the reaction of Bertram and Walbaum,[4] the addition of acetic acid, in presence of mineral acids, I have been led to a somewhat different conception of the camphene molecule.

Camphene and pinene yield the acetates of isoborneol and terpineol, respectively. As regards other terpenes, but little appears to have been published, and I have made the following experiments.

1. *Pinene*, from American turpentine (sp. gr. 0.867. $\alpha_D = + 11°$). 50 cc. with 100 cc. pure acetic acid, containing 1 per cent. sulphuric acid, allowed to stand at 15°-20° for five days. Quantitative saponification showed 43 per cent. terpineol acetate.

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[1] Read before the New York Section of the American Chemical Society, February 7, 1902.

[2] *Ber. d. chem. Ges.*, (1893), p. 3056.

[3] *Ibid.*, (1900), p. 3421.

[4] *J. prakt. Chem.*, **49**, 1.